Phosphato–Titanium Coordination Chemistry. New Phosphato-Bridged Chlorotitanium, Imidotitanium, and Oxotitanium Compounds

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Bis(trimethylsilyl) phosphate and bis(*tert*-butyl) phosphate make tractible crystalline compounds with certain titanium precursor compounds. We have prepared a bis(μ-chloro)(μ-phosphato)titanium compound $Ti_2Cl_7(O_2P(OSiMe_3)_2)(OP(OSiMe_3)_3)$ (**1**), a series of terminal imidotitanium compounds $[R'N{=}Ti(O_2P(OR)_2)_4Ti{=}NR']$ (**2a**, R = ^{t}Bu, R′ = ^{t}Bu; **2b**, R = SiMe$_3$, R′ = ^{t}Bu; **2c**, R = SiMe$_3$, R′ = *tert*-amyl), and a oxotitanium tetramer $[TiO(OSiMe_3)(O_2P(O^tBu)_2)]_4$ (**3**). These compounds all contain phosphate bridges and are possible models for energetically-accessible titanium–phosphate structures not yet observed in extended "inorganic" solids. Compounds **1** and **2b** have been crystallographically characterized: Compound **1**, monoclinic, space group $P2_1/n$ (No. 14), a = 22.376 (4) Å, b = 19.967 (6) Å, c = 9.742 (3) Å, β = 93.25 (2)°, T = −85 °C, Z = 4, R = 0.047, R_w = 0.045; compound **2b**, tetragonal, space group $I4_1/a$ (No. 88), a = 20.829 (4) Å, c = 31.411 (3) Å, T = −100 °C, Z = 8, R = 0.048, R_w = 0.041. Compounds **2** are synthesized from imido-bridged dimeric compounds $[(Me_2N)_2Ti(\mu\text{-}NR')]_2$; when the phosphato groups are introduced in the syntheses of compounds **2**, the bridging imido groups assume terminal positions through a mechanism which probably involves monomeric intermediates.

Introduction

Detailed study of many samples of the important nonlinear optical material "KTP" (potassium titanyl phosphate, $KTiOPO_4$) has addressed some of the questions concerning crystal defects and their importance in, for example, conductivity and laser damage.[1] But a deeper understanding of defects in KTP requires that we know about more than KTP itself; we need to know about *alternatives* to the KTP structure, which is shown schematically in Figure 1.[2] We need to know what other low-energy structures and bonding patterns are available for titanyl–phosphate compounds and how they behave chemically and physically. To this end we have been exploring phosphato–titanium chemistry and report here the preparation and structures of several new compounds.

Phosphato–titanium esters have been used as flame retardants and hardening agents,[3] but typically these compounds are noncrystalline and incompletely structurally characterized. We have found that trimethylsilyl and *tert*-butyl phosphates can yield tractible crystalline compounds when reacted with soluble titanium precursor compounds; in this article we describe three families of product compounds that we have studied to date. These product compounds have some lessons to teach about broader aspects of phosphato–titanium chemistry and at the same time exhibit features of current interest: The chloro compound $Ti_2Cl_7(O_2P(OSiMe_3)_2)(OP(OSiMe_3)_3)$ (**1**) illustrates the initial product of the reaction between Ti compounds and phosphates, compounds $[R'N{=}Ti(O_2P(OR)_2)_2]_2$ (**2**) are the first examples of dimeric titanium compounds with nonbridging imido groups, and the oxo compound $[TiO(SiMe_3)(O_2P(O^tBu)_2)]_4$ (**3**) combines bridging phosphates and oxides to make an unusual cluster.

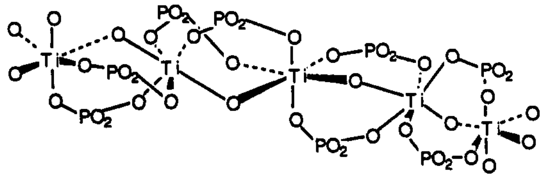
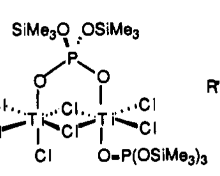


Figure 1. Sketch of part of the crystal structure of potassium titanyl phosphate, KTP. See refs 1 and 2.



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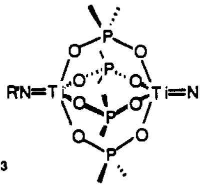

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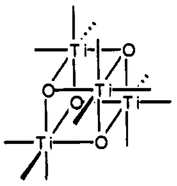

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Results

The three families of phosphato–titanium compounds that we describe are all prepared by elimination reactions, generalized in eq 1. All the stable compounds we have characterized have

$$2\ R_nTiX + OP(OR')(OR'')_2 \rightarrow R'X + R_nTi(O_2P(OR'')_2)TiXR_n \quad (1)$$
$$\downarrow$$
$$\text{etc.}$$

phosphates bridging two titanium centers, and we write eq 1 accordingly. However, it will be seen below that monomeric nonbridged compounds are implicated as reaction intermediates if not as stable products.

$Ti_2Cl_7(O_2P(OSiMe_3)_2)(OP(OSiMe_3)_3)$ (1). This compound is obtained from the $ClSiMe_3$ elimination reaction between $OP(OSiMe_3)_3$ and $TiCl_4$, as in eq 2. Compound **1** is relatively stable in dilute solution or in the presence of excess $ClSiMe_3$ but can undergo further condensation to form oligomeric materials. It is extremely moisture-sensitive with very reactive Ti–Cl bonds, but we have not identified tractible derivative compounds. The structure of compound **1** (Figure 2) reveals a phosphate-bridged Ti_2Cl_2 core having distances and angles (see Tables I and II) that

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† Contribution No. 6138.

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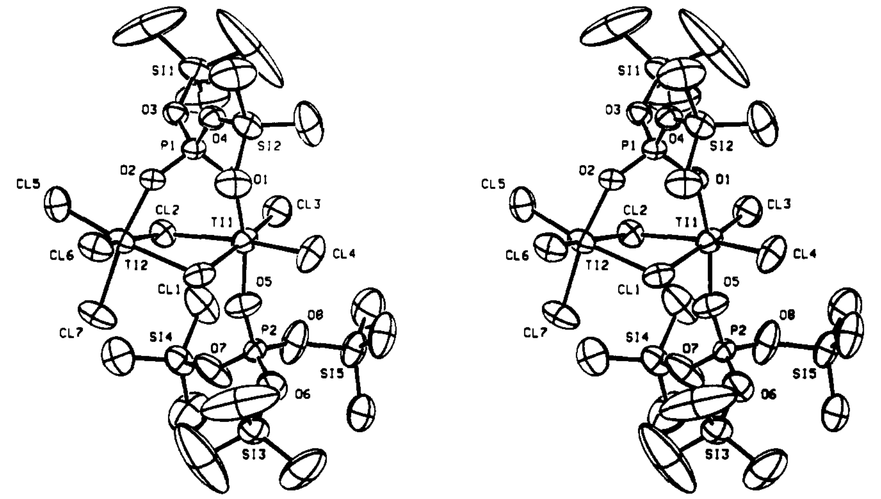
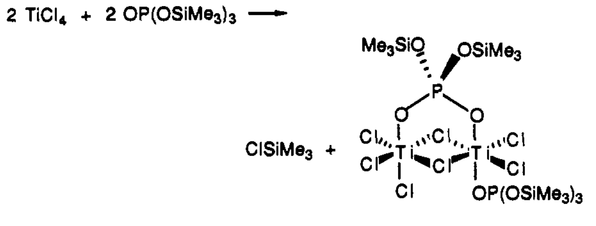


Figure 2. Stereodrawing of compound **1**, $Ti_2Cl_7(O_2P(OSiMe_3)_2)(OP(OSiMe_3)_3)$. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are not included, and the labels on carbon atoms are omitted for clarity.



(2)

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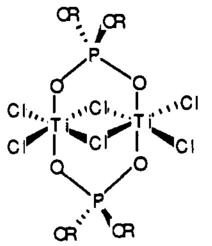
compare well with those of a related adduct of $TiCl_4$, namely $Ti_2Cl_8(POCl_3)_2$.[4] The phosphate bridge of compound **1** causes "hinging" at the bridging chlorides and prevents the second phosphate from bridging in a hypothetical structure of higher symmetry, **4**.



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$[R'N{=}Ti(O_2P(OR)_2)_2]_2$ (2) (2a, R = ^{t}Bu, R′ = ^{t}Bu; 2b, R = $SiMe_3$, R′ = ^{t}Bu; 2c, R = $SiMe_3$, R′ = *tert*-Amyl). These imidotitanium compounds are obtained by Me_2NSiMe_3 elimination from $OP(OSiMe_3)(OR)_2$ and $[(Me_2N)_2Ti(\mu\text{-}NR')]_2$.[5,6] The reaction is very slow at room temperature and requires heating to ca. 60 °C for completion but is very clean and no intermediates or byproducts are observable by NMR spectroscopy. In situ yields are essentially quantitative but crystallization from the reaction solution is inefficient and isolated yields seldom exceed ca. 50%. However, when obtained pure, crystals of compounds **2** are only sluggishly soluble in inert solvents (alkanes, ethers, aromatic hydrocarbons).

Surprisingly the imido groups, which symmetrically bridge the Ti centers in $[(Me_2N)_2Ti(\mu\text{-}NR')]_2$,[5] are terminally bound in compounds **2**, as revealed by the structure determination of compound **2b** (R = $SiMe_3$, R′ = ^{t}Bu) (Figure 3). The Ti–N separation, 1.667 (5) Å (see Table III and the cautionary notes in the Discussion and Experimental Section below), is small compared with other terminal titanium imido compounds (1.719 (3),[7] 1.720 (2),[8] 1.723 (2),[9] 1.702 (4),[10] 1.699 (4),[10] and 1.672 (7)[11] Å), and the Ti–N–C linkage is nearly linear (175.3 (5)°; see Table IV).

Table I. Selected Interatomic Distances (Å) for Compound 1

Ti(1)–Cl(1)	2.506 (2)	P(1)–O(2)	1.506 (3)
Ti(1)–Cl(2)	2.459 (2)	P(1)–O(3)	1.527 (3)
Ti(1)–Cl(3)	2.217 (2)	P(1)–O(4)	1.534 (3)
Ti(1)–Cl(4)	2.228 (2)	P(2)–O(5)	1.440 (4)
Ti(2)–Cl(1)	2.459 (2)	P(2)–O(6)	1.501 (4)
Ti(2)–Cl(2)	2.567 (2)	P(2)–O(7)	1.505 (4)
Ti(2)–Cl(5)	2.240 (2)	P(2)–O(8)	1.506 (4)
Ti(2)–Cl(6)	2.228 (2)		
Ti(2)–Cl(7)	2.247 (2)	Si(1)–O(3)	1.691 (3)
		Si(2)–O(4)	1.697 (3)
Ti(1)–O(1)	1.905 (3)	Si(3)–O(6)	1.705 (4)
Ti(1)–O(5)	1.928 (4)	Si(4)–O(7)	1.695 (4)
Ti(2)–O(2)	1.952 (3)	Si(5)–O(8)	1.707 (4)
P(1)–O(1)	1.519 (3)		

Table II. Selected Intramolecular Angles (deg) for Compound 1

Cl(1)–Ti(1)–Cl(2)	80.16 (6)	Cl(2)–Ti(1)–O(1)	85.2 (1)
Cl(1)–Ti(1)–Cl(3)	173.37 (8)	Cl(2)–Ti(1)–O(5)	85.9 (1)
Cl(1)–Ti(1)–Cl(4)	87.16 (7)	Cl(3)–Ti(1)–O(1)	94.6 (1)
Cl(2)–Ti(1)–Cl(3)	93.45 (6)	Cl(3)–Ti(1)–O(5)	92.4 (1)
Cl(2)–Ti(1)–Cl(4)	167.32 (8)	Cl(4)–Ti(1)–O(1)	94.0 (1)
Cl(3)–Ti(1)–Cl(4)	99.23 (8)	Cl(4)–Ti(1)–O(5)	93.2 (1)
Cl(1)–Ti(2)–Cl(2)	78.97 (6)	Cl(1)–Ti(2)–O(2)	84.1 (1)
Cl(1)–Ti(2)–Cl(5)	166.71 (7)	Cl(2)–Ti(2)–O(2)	83.4 (1)
Cl(1)–Ti(2)–Cl(6)	92.82 (7)	Cl(5)–Ti(2)–O(2)	91.4 (1)
Cl(1)–Ti(2)–Cl(7)	88.02 (7)	Cl(6)–Ti(2)–O(2)	91.9 (1)
Cl(2)–Ti(2)–Cl(5)	88.12 (6)	Cl(7)–Ti(2)–O(2)	168.9 (1)
Cl(2)–Ti(2)–Cl(6)	170.9 (1)	O(1)–Ti(1)–O(5)	169.0 (2)
Cl(2)–Ti(2)–Cl(7)	87.48 (6)	Ti(1)–Cl(1)–Ti(2)	98.12 (6)
Cl(5)–Ti(2)–Cl(6)	99.82 (7)	Ti(1)–Cl(2)–Ti(2)	96.48 (6)
Cl(5)–Ti(2)–Cl(7)	94.60 (8)	O(1)–P(1)–O(2)	111.0 (2)
Cl(6)–Ti(2)–Cl(7)	96.25 (7)	Ti(1)–O(1)–P(1)	140.6 (2)
Cl(1)–Ti(1)–O(1)	86.7 (1)	Ti(2)–O(2)–P(1)	142.0 (2)
Cl(1)–Ti(1)–O(5)	85.4 (1)	Ti(1)–O(5)–P(2)	164.4 (3)

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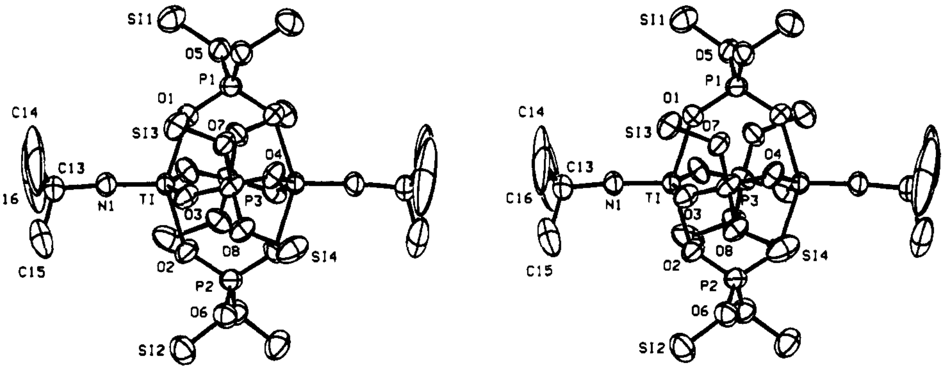


Figure 3. Stereodrawing of compound **2b**, $[{}^tBuN{=}Ti(O_2P(OSiMe_3)_2)_2]_2$. Thermal ellipsoids are drawn at the 25% probability level. Hydrogen atoms and trimethylsilyl carbon atoms are omitted for clarity. Atoms P(1) and P(2) sit on a crystallographic 2 axis; the molecular core has approximate D_4 symmetry.

Table III. Selected Interatomic Distances (Å) for Compound **2b**

Ti(1)–O(1)	2.030 (4)	P(3)–O(8)	1.570 (4)
Ti(1)–O(2)	2.025 (4)	Si(1)–O(5)	1.672 (4)
Ti(1)–O(3)	2.034 (4)	Si(2)–O(6)	1.659 (4)
Ti(1)–O(4)^a	2.030 (4)	Si(3)–O(7)	1.681 (4)
		Si(4)–O(8)	1.665 (4)
Ti(1)–N(1)	1.667 (5)		
		N(1)–C(13)	1.444 (7)
P(1)–O(1)	1.496 (4)		
P(1)–O(5)	1.562 (4)	C(13)–C(14)	1.396 (12)
P(2)–O(2)	1.497 (4)	C(13)–C(15)	1.470 (11)
P(2)–O(6)	1.563 (4)	C(13)–C(16)	1.449 (12)
P(3)–O(3)	1.502 (4)		
P(3)–O(4)	1.498 (4)	Ti(1)---Ti(1)^a	3.658 (2)
P(3)–O(7)	1.556 (4)		

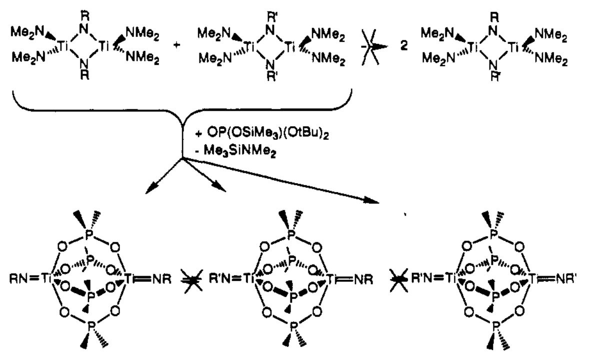
^{a} Symmetry operation code: $1 - x, {}^1/_2 - y, z$.

Table IV. Selected Intramolecular Angles (deg) for Compound **2b**

O(1)–Ti(1)–O(2)	145.7 (2)	O(2)–P(2)–O(2)^a	115.4 (4)
O(1)–Ti(1)–O(3)	85.0 (2)	O(3)–P(3)–O(4)	115.6 (2)
O(1)–Ti(1)–O(4)	85.1 (2)		
O(2)–Ti(1)–O(3)	84.6 (2)	Ti(1)–O(1)–P(1)	135.0 (3)
O(2)–Ti(1)–O(4)	85.5 (2)	Ti(1)–O(2)–P(2)	136.2 (3)
O(3)–Ti(1)–O(4)	145.9 (2)	Ti(1)–O(3)–P(3)	132.0 (3)
O(1)–Ti(1)–N(1)	108.3 (2)	Ti(1)^a–O(4)–P(3)	139.4 (3)
O(2)–Ti(1)–N(1)	106.0 (2)		
O(3)–Ti(1)–N(1)	107.0 (2)	Ti(1)–N(1)–C(13)	175.3 (5)
O(4)^a–Ti(1)–N(1)	107.1 (2)	N(1)–C(13)–C(14)	110.6 (7)
		N(1)–C(13)–C(15)	109.6 (6)
O(1)–P(1)–O(1)^a	116.0 (3)	N(1)–C(13)–C(16)	110.3 (7)

^{a} Symmetry operation code: $1 - x, {}^1/_2 - y, z$.

We were intrigued by the bridge → terminal conversion of the imido groups in the formation of compounds **2**. In an effort to learn more about this process we prepared the compound $[(Me_2N)_2Ti(\mu\text{-}N\text{-}\mathit{tert}\text{-}amyl)]_2$ and used mixtures of it and $[(Me_2N)_2Ti(\mu\text{-}N^tBu)]_2$ in crossover studies. Our findings are summarized below and in eq 3.



(3)

(1) Mixtures of the unscrambled terminal imido compounds $[R'N{=}Ti(O_2P(OSiMe_3)_2)_2]_2$ (R′ = ^{t}Bu, **2b**; R′ = *tert*-amyl, **2c**) produced *no* scrambled compound, even when heated to 60 °C with excess silyl phosphate reagent.

(2) An equimolar mixture of the unscrambled imido-bridged compounds $[(Me_2N)_2Ti(\mu\text{-}N^tBu)]_2$ and $[(Me_2N)_2Ti(\mu\text{-}N\text{-}\mathit{tert}\text{-}amyl)]_2$, when reacted with $OP(OSiMe_3)_3$ in C_6D_6 at room temperature or at 60 °C (ca. 1 h), *did* produce a mixture of scrambled terminal imido compounds **2** $[R'N{=}Ti(O_2P(OSiMe_3)_2)_4Ti{=}NR'']$ (R′, R″ = ^{t}Bu, *tert*-amyl), characterized by ^{31}P NMR spectroscopy (see Experimental Section). The products were not formed in rigorously statistical amounts, and there was a slight preference for the *tert*-butylimido compound **2b**, probably owing to steric effects.

(3) After experiment 2 above the remaining unreacted imido-bridged compounds were not scrambled. It was confirmed that when an equimolar mixture of the imido-bridged starting compounds $[(Me_2N)_2Ti(\mu\text{-}N^tBu)]_2$ and $[(Me_2N)_2Ti(\mu\text{-}N\text{-}\mathit{tert}\text{-}amyl)]_2$ in C_6D_6 was heated to 60 °C, *no* scrambled product could be detected (^1H NMR). A mixture containing the scrambled imido-bridged compound $[(Me_2N)_2Ti(\mu\text{-}N^tBu)(\mu\text{-}N\text{-}\mathit{tert}\text{-}amyl)Ti(NMe_2)_2]$ was formed separately from the reaction between $Ti(NMe_2)_4$ and equimolar *tert*-butylamine/*tert*-amylamine, and its detectability by ^1H NMR was confirmed (see Experimental Section).

Thus, it is *only* during the *formation* of terminal imido compounds **2** that scrambling can occur. This leads us to propose that monomeric nonbridged compounds $R'N{=}Ti(Me_2N)_{2-x}(O_2P(OR)_2)_x$ (x = 1 or 2 but not 0) are intermediates in the formation of compounds **2**.

Compounds **2** react with aldehydes, and the organic *tert*-butylimine is formed slowly when compound **2b** is treated with *p*-tolualdehyde at room temperature. The reaction with benzaldehyde is somewhat faster, and when followed by UV–visible absorption spectra, the disappearance of compound **2b** in benzene with excess benzaldehyde (initial concentrations 0.0014 M compound **2b**, 0.078 M benzaldehyde) is first order, $t_{1/2}$ at room temperature 173 (5) min. However, by NMR spectroscopy the reaction forms a mixture of metal products which we have not been able to separate or characterize further. Presumably the initial product contains terminal Ti═O groups but these oligomerize and/or displace phosphate bridges and/or silyl groups. Likewise, compounds **2** react with primary amines but the products have not been identified. Reactions with olefins, acetylenes, or C–H bonds have not been observed.

The four bridging phosphate ligands give these compounds a striking structural resemblance to the "PtPOP" compounds, which have long-lived electronic excited states exhibiting rich photochemistry.[12] Remarkably, compounds **2** also have long-lived excited states and luminesce yellow-orange at room temperature in both the solid state and in solution. The emission spectrum of **2b** (R = $SiMe_3$, R′ = ^{t}Bu) in benzene at room temperature

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[12] See, e.g.: Zipp, A. P. *Coord. Chem. Rev.* **1988**, *84*, 47–83.

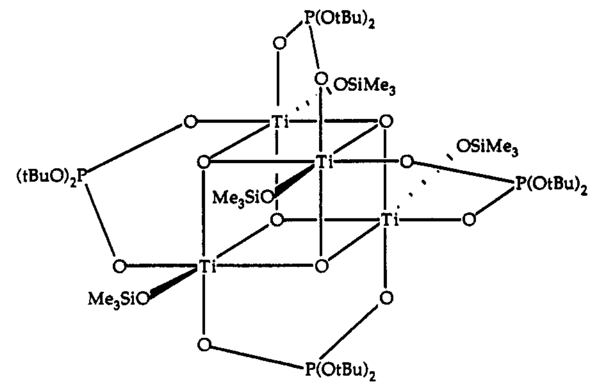
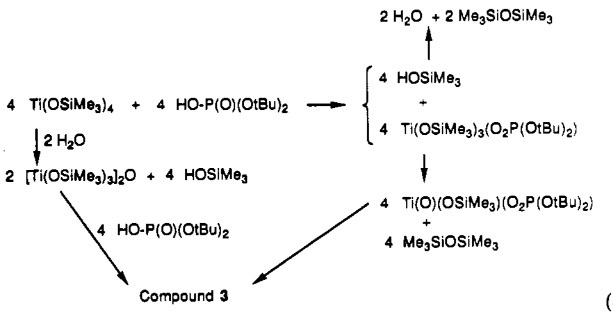


Figure 4. Sketch of compound **3**, $[TiO(OSiMe_3)(O_2P(O^tBu)_2)]_4$. The molecular core has approximate D_{2d} symmetry.

is essentially Gaussian, with a maximum at 650 nm (excitation at 430 nm) and approximately 60-nm wide at half-height; the excited-state lifetime is 12.5 μs in tetrahydrofuran solution. The electronic absorption spectra of compounds **2** have a peak at 395 nm (ϵ = 450 L mol^{-1} cm^{-1} in benzene) on the side of a much more intense absorption at higher energy, giving rise to their observed yellow color. The excited state may involve N–Ti charge transfer and/or metal–metal bonding, but the exact nature has not been established.[13]

$[TiO(OSiMe_3)(O_2P(O^tBu)_2)]_4$ (3). This compound is obtained from the reaction between $Ti(OSiMe_3)_4$ and $OP(OH)(O^tBu)_2$ in hexane at room temperature. The reaction requires several hours, and when it is monitored by ^{1}H NMR spectroscopy (C_6D_6), several unidentified intermediate compounds are observed. The reaction has been run successfully on a scale sufficiently large that the primary source of the oxo oxygen atom is unlikely to be adventitious water or air. Thus, we believe the oxo oxygen atom comes from siloxide; water may indeed be involved, but if so, it comes from the condensation of trimethylsilanol in, for example, the hypothetical reaction sequence of eq 4. Attempts to prepare



(4)

compound **3** by hexamethyldisiloxane elimination from $Ti(OSiMe_3)_4$ and $OP(OSiMe_3)(O^tBu)_2$ have failed; likewise attempts to prepare the related silyl phosphate compound $[TiO(OSiMe_3)(O_2P(OSiMe_3)_2)]_4$ have been unsuccessful.

The structure of compound **3** is shown schematically in Figure 4, as derived from single-crystal X-ray diffraction data. Unfortunately, single crystals of the compound contain solvent (hexane) and diffract poorly even at –70 °C, and the data set is of limited quality; we have abandoned further attempts to refine the obviously disordered structure after obtaining $R = 0.135$.

The $[TiO(OSi)(O_2P)]_4$ core is unambiguously defined, but interatomic distances and angles are not known with any meaningful accuracy.

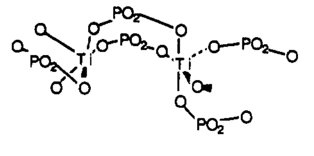
Compound **3** is remarkably stable; for instance it is insoluble in and has been recovered unchanged from boiling methanol and is unaffected by traces of moisture. We have observed reactions of compound **3** with potassium *tert*-butoxide, with $(Me_2N)_3S^+F_2SiMe_3^-$, and with phenol, but the products have not been characterized.

Discussion

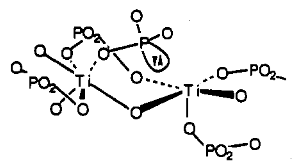
These three families of compounds illustrate a general trend: Phosphates make very stable complexes with and exhibit distinct tendencies to bridge titanium centers, even in the absence of other bridging groups or atoms. Indeed, a search of the Cambridge Crystal Database[14] reveals 95 structures of the form M–O–PR$_2$–O–M′ (R = alkyl, alkoxide, hydroxide, halide) but only 7 structures having –O–PR$_2$–O– ligands chelating a single metal center. Thus the bridging tendency of oxy–phosphorus compounds encompasses the entire set of transition metals and defines a property inherent to phosphato ligands, the utility of which remains to be fully exploited in coordination and organometallic chemistry.

Compound **1** was obtained when $TiCl_4$ was combined with tris(trimethylsilyl) phosphate. We had expected the evolution of $ClSiMe_3$ to be complete and to form compounds such as $(Cl_3TiO)_3POTiCl_4$, where the phosphato group is bound to four titanium centers and could mimic the phosphato group of KTP. Unexpectedly, $ClSiMe_3$ evolution is rapid at room temperature only until compound **1** is formed with further $ClSiMe_3$ evolution being somewhat slower. (In this respect the reaction resembles the reaction between $TiCl_4$ and $N(SiMe_3)_3$.[15]) While compounds such as $(Cl_3TiO)_3POTiCl_4$ may indeed be formed eventually, so are other compounds, and separation/identification has not been successful.

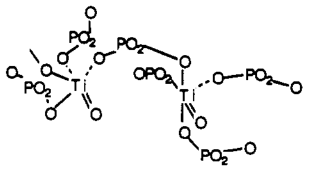
Compounds **2** are especially relevant to our interest in KTP and alternate structures. KTP crystals as typically grown using high-temperature flux techniques have ca. several hundred ppm of oxygen vacancies, most of which are believed to be located between adjacent Ti centers—i.e. it is the "titanyl" oxygen that can be missing (**5a**) not the "phosphate" oxygen (**5b**).[1] Thus, the site of the missing titanyl oxygen consists of two pentacoordinate Ti centers. The usual coordination of Ti(IV) in "inorganic" ligand environments is octahedral so the proposed oxygen defect sites in the KTP structure (**5a**) appear at first glance to be energetically unfavorable. But pentacoordinate titanium in an environment of O-donors is well-known (see, e.g., ref 13 and references therein;



5a



5b



5c

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(13) Long-lived excited states are known for other metal–oxo, –imido, and –nitrido compounds. See e.g.: Yam, V. W.-W.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1990**, 3741–3746 and references therein. Pollagi, T. P.; Stoner, T. C.; Dallinger, R. F.; Gilbert, T. M.; Hopkins, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 703–704. Neyhart, G. A.; Seward, K. J.; Boaz, J.; Sullivan, B. P. *Inorg. Chem.* **1991**, *30*, 4486–4488. Caspar, J. V.; Nugent, W. A. Personal communication. Luminescence of solid titanates is surveyed in: Blasse, G. Luminescence and Energy Transfer. *Structure and Bonding*, Vol. 42; Springer-Verlag: Berlin, 1980, pp 1–41. We thank M. G. Roelofs for bringing this work to our attention.

(14) We searched the 1/91 release of the Cambridge Database. The numbers of "hits" we report should be viewed as indicative but not definitive, as some structures should be included in several related categories.

(15) Alcock, N. W.; Pierce-Butler, M.; Wiley, G. R. *J. Chem. Soc., Dalton Trans.* **1976**, 707–713.

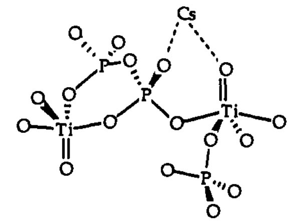
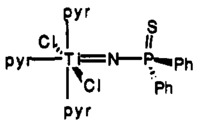


Figure 5. Sketch of part of the crystal structure of $Cs_2TiO(P_2O_7)$. See ref 16.

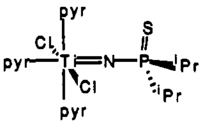
see also refs 7 and 11). Also, recently a phosphato–titanium(IV) compound was reported, $Cs_2TiO(P_2O_7)$[16] (see Figure 5),having pentacoordinate Ti(IV) with a terminal (nonbridging) oxo (Ti–O = 1.644 (4) Å) (**5c**). Noting the frequently-drawn analogy between oxo and imido ligands,[17] we assert that the compounds **2** are molecular analogs of the Ti center of $Cs_2TiO(P_2O_7)$. Together these provide support for the proposed oxygen defect site of KTP itself and demonstrate that Ti(IV) in a phosphato environment easily tolerates pentacoordination and can support terminal (nonbridging) oxo/imido ligands.

Six other terminally-bound imidotitanium compounds (**6a**, **6b**, **7–10**) have been reported recently,[7-11] all having somewhat greater Ti=N distances (respectively 1.720 (2), 1.723 (2), 1.719 (3), 1.699 (4), 1.702 (4), 1.672 (7) Å) than our compound **2b** (1.667 (5) Å). However, we note that the crystal structure determination of compound **2b** may be compromised by crystal decomposition (see Experimental Section) and derived distances and angles should be viewed with caution. Despite this decomposition we believe that the Ti=N distance as derived from our data (1.667 (5) Å, Table III) is a reasonable estimate of the "true" distance and that this distance is among the shortest of the known terminal imidotitanium compounds. At least four factors contribute to establishing the Ti=N distance, illustrating the complexity of the structural details of metal-ligand multiple bonds.[17]

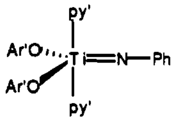
(1) The titanium centers in compounds **2** are strictly pentacoordinate, and the vacant sixth coordination site (trans to the imido group) is totally inaccessible (see Figure 3) (the Ti- - -Ti distance, 3.658 (2) Å, does not suggest any significant metal–metal interaction in the ground electronic state). The imidotitanium compounds **6a**[8] and **6b**[9] each have a sixth ligand, a pyridine bound trans to the imido group (Ti–N(pyr) = 2.439 (2) Å in compound **6a** and 2.415 (2) Å in compound **6b**), which is expected to lengthen the Ti=NR bond.



6a



6b



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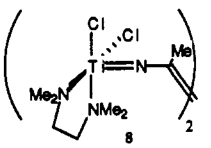

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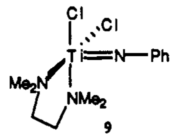

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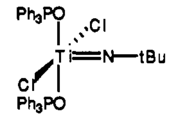

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(2) The titanium centers in compounds **2** have only phosphato oxygen atoms as supporting ligands, and their π-donating capacity appears to be minimal; the O–Ti bond distances are all between 2.025 (4) and 2.034 (4) Å (see Table III). Thus, the imido nitrogen atom enjoys maximum π-bonding with the titanium and does not compete with other π-donors. The imidotitanium compound **7**[7] has two pyridinyl and two phenolic ligands, the latter being good π-donors (average Ti–O = 1.87 Å) that compete with the imido nitrogen atom for π-bonding with the titanium center.

(3) The titanium centers in compounds **2** are best described as square pyramidal with average N–Ti–O angles of 107 (1)° and average trans O–Ti–O angles of 145.8 (3)° (Table IV). The imidotitanium compound **7**[7] is better described as a trigonal bipyramid with average N(imido)–Ti–O(phenolate) angles 113° and a trans O–Ti–O angle 133.2 (1)°. Thus, the phenolate oxygens in compound **7** are more nearly trans to the imido group and are expected to lengthen the Ti=NR bond.

(4) Compounds **8**, **9**,[10] and **10**,[11] like our compounds **2**, contain square-pyramidal five-coordinate Ti centers with supporting ligands having minimal π-donation capacity and have relatively short Ti=N bonds (1.699 (4) Å for compound **8**, 1.702 (4) Å for compound **9**, 1.672 (7) Å for compound **10**). But compounds **8** and **9**, indeed **6** and **7** as well, have groups bonded to the imido nitrogen atom which are capable of formal resonance delocalization of the Ti=N multiple bond, whereas compounds **2** and **10** have no formal resonance delocalization.

Reactions undergone by the imidotitanium compounds **6**, **7**, and **9** have not been described; the remarkable hydrolytic formation of tetramethylpyrazine from compound **8** warrants further study. It will be interesting to compare reactivities among these various imidotitanium compounds and $[(Me_2N)_2Ti(\mu\text{-}NR)]_2$ although it is unlikely that any will exhibit the extreme reactivity of coordinatively-unsaturated imidozirconium[18] or -titanium compounds;[19] indeed, compound **7** is referred to by its discoverers as a "dead dog".[7b] The imidotitanium compounds we describe and also compounds **6** and **7** resist low coordination numbers and are correspondingly relatively unreactive. This is particularly apparent in the compounds $[(Me_2N)_2Ti(\mu\text{-}NR)]_2$, where monomeric species are not formed even at 60 °C, as revealed by their unobservably slow rate of scrambling,[20] although we do postulate monomeric Ti compounds as intermediates in the formation of compounds **2** (see above). Bulky ligands, labile ligands, and/or conditions favoring low coordination number seem to be necessary to promote the reactivity of the imidotitanium group, and compounds **8** and **9** are particularly promising in this regard. One reaction we have observed for compounds **2**, the metathesis reaction with aldehydes, is consistent with the correlation noted between metathesis reactivity and ^{13}C chemical shifts of *tert*-butylimido groups,[17,21] although this reaction of **2** probably requires dissociation of a $Ti\text{–}OPO(OR)_2$ bond.

Compound **3** is structurally similar to the well-known "cubane" $M_4(\mu\text{-}X)_4$ cluster compounds, although such a "cubane" structure is rare for molecular oxotitanium compounds. A closely related oxo(imido)rhenium cluster has been reported recently[22] and phosphato-bridged "cubane" entities are present in molybdenum phosphate structures.[23] Other μ_3-oxo bridges are known in molecular Ti chemistry (see, for example, the oxo–acetato–titanium compounds in ref 24 and the oxo–cyclopentadienyl–titanium compound of ref 25), but the more usual (μ-oxo)titanium compounds have only doubly-bridging oxo atoms (e.g. the KTP

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Table V. NMR Data (ppm) for **2b**, **2c**, Precursors, and Crossover Products

	$\mathrm{N(C}H_3)_2$	$\mathrm{NC(C}H_3)_3$	$\mathrm{NC(Et)(C}H_3)_2$	$\mathrm{NC(C}H_2\mathrm{CH_3)Me_2}$	$\mathrm{NC(CH_2C}H_3\mathrm{)Me_2}$
$[(\mathrm{Me_2N})_2\mathrm{Ti}(\mathrm{N^tBu})]_2$	3.36	1.16			
$[(\mathrm{Me_2N})_2\mathrm{Ti}$(N-*tert*-amyl)$]_2$	3.36		1.13	1.32 q (7.5)	0.90 t (7.5)
$(\mathrm{Me_2N})_2\mathrm{Ti}(\mu\text{-}\mathrm{N^tBu})$($\mu$-N-*tert*-amyl)$\mathrm{Ti(NMe_2)_2}$	3.36	1.17	1.12	1.30 q (7.5)	0.90 t (7.5)
$\mathrm{Me_3CN{=}Ti(O_2P(OSiMe_3)_2)_4Ti{=}NCMe_3}$ (**2b**)^a		1.11			
$\mathrm{Me_2EtCN{=}Ti(O_2P(OSiMe_3)_2)_4Ti{=}NCMe_2Et}$ (**2c**)^b			1.09	1.29 q (7)	1.15 t (7)
$\mathrm{Me_3CN{=}Ti(O_2P(OSiMe_3)_2)_4Ti{=}NCMe_2Et}^c$		1.11	1.09	1.29 q (7)	1.15 t (7)

^{a} $\mathrm{Si(CH_3)_3}$, 0.51 ppm; $\{^1\mathrm{H}\}^{31}\mathrm{P}$, –15.11 ppm. ^{b} $\mathrm{Si(CH_3)_3}$, 0.51 ppm; $\{^1\mathrm{H}\}^{31}\mathrm{P}$, –15.23 ppm. ^{c} $\mathrm{Si(CH_3)_3}$, 0.51 ppm; $\{^1\mathrm{H}\}^{31}\mathrm{P}$, –15.18 ppm.

structure; see Figure 1 and ref 26). Among "inorganic" Ti compounds, the "cubane" core of compound **3** resembles the anatase form of $\mathrm{TiO_2}$.[27] In this respect, compound **3** may model the surface species when a particle of anatase is exposed to phosphate; phosphate stabilization of the "cubane" structure may help explain the effect of phosphate in retarding the anatase → rutile transformation.[28]

Summary

Our exploration of phosphato–titanium compounds has revealed an unexpectedly diverse field of molecular coordination chemistry. Perhaps the most interesting compounds we have identified are the imido compounds **2**: Compounds **2** demonstrate that the very simple "inorganic" phosphate ligand can support imido groups (and perhaps other functional groups relevant to organic chemistry and to catalysis), as well as helping demonstrate the viability of the proposed oxygen-defect site of KTP.

Experimental Section

Caution: Chlorotrimethylsilane ($\mathrm{ClSiMe_3}$) is a suspected carcinogen, and it, as well as the other trimethylsilyl compounds, should be treated with care!

All reactions were carried out using dried solvents and standard inert-atmosphere techniques. NMR data were obtained using GE QE300 instruments at ambient probe temperatures; chemical shifts are reported in ppm downfield from external standards ($\mathrm{Si(CH_3)_4}$ for $^1\mathrm{H}$ and $^{13}\mathrm{C}$, 85% $\mathrm{H_3PO_4}$ for $^{31}\mathrm{P}$) with coupling constants in Hz, integrals, or assignments in parentheses. Elemental analyses were performed by Galbraith Laboratories. The compounds $[(\mathrm{Me_2N})_2\mathrm{Ti}(\mu\text{-}\mathrm{NR'})]_2$ (R' = *tert*-butyl, *tert*-amyl)[5,6] and $\mathrm{(HO)P(O)(O^tBu)_2}$[29] were prepared following literature methods. The compounds $\mathrm{OP(OSiMe_3)_3}$ and $\mathrm{Ti(OSiMe_3)_4}$ were obtained commercially.

Preparation of $\mathrm{Ti_2Cl_7(O_2P(OSiMe_3)_2)(OP(OSiMe_3)_3)}$ (1). A solution of 0.16 g (0.51 mmol) of $\mathrm{OP(OSiMe_3)_3}$ and 0.095 g (0.50 mmol) of $\mathrm{TiCl_4}$ in 1 mL of $\mathrm{ClSiMe_3}$ was boiled gently for 5 min. The resulting yellow solution was allowed to cool, eventually depositing 0.15 g of pale yellow crystalline solid compound **1** (0.167 mmol, 66%). The material shows extreme moisture-sensitivity. NMR ($\mathrm{C_6D_6}$): $^1\mathrm{H}$, 0.23 s (27 H), 0.29 s (18 H); $\{^1\mathrm{H}\}^{31}\mathrm{P}$, –26.8, –35.2.

In a separate experiment, 0.16 g of $\mathrm{OP(OSiMe_3)_3}$ and 0.10 g of $\mathrm{TiCl_4}$ were combined in $\mathrm{C_6D_6}$, and the solution was briefly heated to boiling; the NMR spectra ($^1\mathrm{H}$, $\{^1\mathrm{H}\}^{31}\mathrm{P}$) revealed compound **1** and $\mathrm{ClSiMe_3}$ in the expected ratios as the dominant components. An additional $^{31}\mathrm{P}$ NMR signal at –33 ppm was apparent, arising from an unidentified reaction component.

Preparation of $[\mathrm{^tBuN{=}Ti(O_2P(O^tBu)_2)_2}]_2$ (2a). The silyl compound $\mathrm{(Me_3SiO)P(O)(O^tBu)_2}$ was prepared by adding 0.63 g (3.0 mmol) of $\mathrm{(HO)P(O)(O^tBu)_2}$ to a stirred solution of 0.31 g of $\mathrm{NEt_3}$ and 0.33 g of $\mathrm{ClSiMe_3}$ in 10 mL of tetrahydrofuran. After being stirred an additional 1 h, the mixture was filtered and the solution evaporated, leaving 0.84 g of cloudy oil (2.97 mmol of crude silyl ester), which solidified when cooled to –30 °C. NMR ($\mathrm{C_6D_6}$): 0.25 s (9 H), 1.43 s (18 H). A solution of 0.58 g (2.05 mmol) of crude $\mathrm{(Me_3SiO)P(O)(O^tBu)_2}$ and 0.21 g of $[(\mathrm{Me_2N})_2\mathrm{Ti}(\mu\text{-}\mathrm{N^tBu})]_2$ (1.01 mmol Ti) in 10 mL of benzene was boiled gently for $^1/_2$ h open to a dinitrogen atmosphere and then concentrated to ca. 5 mL and allowed to stand overnight at room temperature. The orange-red solution deposited large yellow crystals of compound **2a**, 0.25 g (0.47 mmol of Ti, 46%), and additional yellow microcrystals were obtained from the solution by further concentration. Anal. Calcd for $\mathrm{C_{40}H_{90}N_2O_{16}P_4Ti_2}$: C, 44.70; H, 8.44; N, 2.61. Found: C, 44.21; H, 8.34; N, 2.49. NMR ($\mathrm{C_6D_6}$): $^1\mathrm{H}$, 1.12 s (9 H), 1.69 s (36 H); $\{^1\mathrm{H}\}^{31}\mathrm{P}$ –9.6 s; $\{^1\mathrm{H}\}^{13}\mathrm{C}$, 30.9 s ($\mathrm{OC}C\mathrm{H_3}$), 31.5 s ($\mathrm{NC}C\mathrm{H_3}$), 72.6 s ($\mathrm{N}C\mathrm{CH_3}$), 80.6 d (7) ($\mathrm{O}C\mathrm{CH_3}$); $\Delta\delta$ 41 ppm.[17,21]

The compound $[\mathrm{^tBuN{=}Ti(O_2P(OSiMe_3)_2)_2}]_2$ (**2b**) was prepared similarly from the reaction between $\mathrm{OP(OSiMe_3)_3}$ and $[(\mathrm{Me_2N})_2\mathrm{Ti}(\mu\text{-}\mathrm{N^tBu})]_2$. NMR parameters are included in Table V. The compound is hydrolytically sensitive. Anal. Calcd for $\mathrm{C_{32}H_{90}N_2O_{16}P_4Si_8Ti_2}$: C, 31.94; H, 7.59; N, 2.33. Found: C, 31.18; H, 7.27; N, 2.27.

The compound [*tert*-amyl-N=$\mathrm{Ti(O_2P(OSiMe_3)_2)_2}]_2$ (**2c**) was prepared similarly from the reaction between $\mathrm{OP(OSiMe_3)_3}$ and $[(\mathrm{Me_2N})_2\mathrm{Ti}$($\mu$-N-*tert*-amyl)$]_2$. NMR parameters are included in Table V.

Crossover Experiments. (1) Pure compound **2b**, $[\mathrm{^tBuN{=}Ti(O_2P(OSiMe_3)_2)_2}]_2$ (0.02 g), and pure compound **2c**, [*tert*-amyl-N=$\mathrm{Ti(O_2P(OSiMe_3)_2)_2}]_2$ (0.02 g), were combined in 2 mL of $\mathrm{C_6D_6}$ with 0.01 g of additional $\mathrm{OP(OSiMe_3)_3}$, and the mixture was separated into two portions. One was heated (60 °C, 1 h) and the other left at room temperature. NMR analysis ($^1\mathrm{H}$, $^{31}\mathrm{P}$) of both revealed only signals of the starting compounds **2b** and **2c** (see Table V) together with unreacted $\mathrm{OP(OSiMe_3)_3}$ ($^{31}\mathrm{P}$, –24.3 ppm), and no additional signal ascribable to the crossover product could be detected.

(2) $[(\mathrm{Me_2N})_2\mathrm{Ti}(\mu\text{-}\mathrm{N^tBu})]_2$, 0.01 g, $[(\mathrm{Me_2N})_2\mathrm{Ti}$($\mu$-N-*tert*-amyl)$]_2$, 0.01 g, and 0.09 g of $\mathrm{OP(OSiMe_3)_3}$ were combined in 2 mL of $\mathrm{C_6D_6}$, and the mixture was separated into two portions. One was heated (60 °C, 1 h) and the other left at room temperature. Both samples had $^{31}\mathrm{P}$ NMR signals at –15.11, –15.18, and –15.22 ppm in approximate ratios 10:6:4; the room-temperature sample had considerable unreacted $\mathrm{OP(OSiMe_3)_3}$ ($^{31}\mathrm{P}$, –24.3 ppm). The $^1\mathrm{H}$ NMR spectra of these samples contained signals of the unreacted, unscrambled, imido-bridged starting materials, but no signals of the scrambled imido-bridged dimer could be discerned (see below and Table V). The $^{31}\mathrm{P}$ NMR signal at –15.18 ppm is assigned to the crossover product [$\mathrm{^tBuN{=}Ti(O_2P(OSiMe_3)_2)_4Ti}$=N-*tert*-amyl] (see Table V) and is also present in the crystalline product of the preparatory-scale reaction between $[(\mathrm{Me_2N})_2\mathrm{Ti}(\mu\text{-}\mathrm{N^tBu})]_2$, $[(\mathrm{Me_2N})_2\mathrm{Ti}$($\mu$-N-*tert*-amyl)$]_2$, and $\mathrm{OP(OSiMe_3)_3}$.

(3) A mixture of 2.20 g (9.81 mmol) of $\mathrm{Ti(NMe_2)_4}$, 0.36 g (4.92 mmol) of *tert*-butylamine, 0.44 g (5.05 mmol) of *tert*-amylamine, and 5 mL of hexane was heated briefly, filtered, allowed to stand at room temperature for 4 days, and then cooled, depositing 0.54 g of crystalline red solid. The $^1\mathrm{H}$ NMR spectrum of this material had signals of $[(\mathrm{Me_2N})_2\mathrm{Ti}(\mu\text{-}\mathrm{N^tBu})]_2$ and $[(\mathrm{Me_2N})_2\mathrm{Ti}$($\mu$-N-*tert*-amyl)$]_2$ (assigned by comparison with authentic samples) together with new signals assigned to the scrambled dimer $[(\mathrm{Me_2N})_2\mathrm{Ti}(\mu\text{-}\mathrm{N^tBu})$($\mu$-N-*tert*-amyl)$\mathrm{Ti(NMe_2)_2}]$ (see Table V). When a solution of $[(\mathrm{Me_2N})_2\mathrm{Ti}(\mu\text{-}\mathrm{N^tBu})]_2$ (0.01 g) and $[(\mathrm{Me_2N})_2\mathrm{Ti}$($\mu$-N-*tert*-amyl)$]_2$ (0.01 g) in $\mathrm{C_6D_6}$ was heated (60 °C, 0.5 h), the $^1\mathrm{H}$ NMR spectrum revealed only signals of the starting materials, and signals of the scrambled dimer $[(\mathrm{Me_2N})_2\mathrm{Ti}(\mu\text{-}\mathrm{N^tBu})$($\mu$-N-*tert*-amyl)$\mathrm{Ti(NMe_2)_2}]$ were absent.

Preparation of $[\mathrm{TiO(OSiMe_3)(O_2P(O^tBu)_2)}]_4$ (3). $\mathrm{Ti(OSiMe_3)_4}$ (3.83 g, 9.46 mmol) and $\mathrm{HOP(O)(O^tBu)_2}$ (1.99 g, 9.47 mmol) were dissolved in 10 mL of hexane, and the solution was stirred at room temperature. A white precipitate formed almost immediately but soon redissolved. After several hours a precipitate formed again; the mixture was cooled and filtered, providing 2.34 g of white solids (1.61 mmol, 68%). NMR ($\mathrm{C_6D_6}$): $^1\mathrm{H}$, 0.51 s, 1.55 s; $\{^1\mathrm{H}\}^{31}\mathrm{P}$, –10.1 s. Single crystals of a hexane solvate were obtained by cooling a warm hexane solution, but hexane is easily lost. Anal. Calcd for $\mathrm{C_{44}H_{108}O_{24}P_4Si_4Ti_4}$: C, 36.47; H, 7.51. Found: C, 36.78, 36.29; H, 7.49, 7.36.

X-ray Data Collection and Structure Refinements. Single crystals of compounds **1**, **2b**, and **3** were obtained from $\mathrm{ClSiMe_3}$, hexane/pentane,

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Table VI. Crystal Structure Information

compd	$Ti_2Cl_7(O_2P(OSiMe_3)_2)(OP(OSiMe_3)_3)$ (**1**)	$[^tBuN{=}Ti(O_2P(OSiMe_3)_2)_2]_2$ (**2b**)
formula	$C_{15}H_{45}O_8Cl_7P_2Si_5Ti_2$	$C_{32}H_{90}N_2O_{16}P_4Si_8Ti_2$
fw	899.89	1203.49
space group	$P2_1/n$ (No. 14)	$I4_1/a$ (No. 88)
a, Å	22.376 (4)	20.829 (4)
b, Å	19.967 (6)	
c, Å	9.742 (3)	31.411 (3)
β, deg	93.25 (2)	
V, Å^3	4345.5	13628.9
T, K	188	173
Z	4	8
λ, Å	0.710 69	0.710 69
D_{calc}, g cm^{-3}	1.383	1.173
μ, cm^{-1} (Mo)	10.42	5.09[a]
$R(F_o)$[b]	0.047	0.048
$R_w(F_o)$[b]	0.045	0.041

[a] Absorption correction (azimuthal) applied, range of transmission factors 0.87–0.94. [b] $R(F_o) = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_w(F_o) = \sum w(|F_o| - |F_c|^2/\sum w|F_o|^2$.

and hexane solutions, respectively. Crystals of compounds **1** and **2b** were mounted on a Syntex R3 diffractometer; an Enraf-Nonius CAD4 diffractometer was used for compound **3**. Both instruments were equipped with graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å) and intensity data were collected using the ω-scan technique. Crystallographic information on compounds **1** and **2b** is provided in Table VI. Compound **1** undergoes a phase transition at ca. −100 °C, perhaps involving orientations of the trimethylsiloxy groups, which show considerable "thermal motion" even at −85 °C. The phase transition produces additional spots on axial photographs of the c-axis indicating that it should be tripled in length. The intensities of these extra reflections were so weak that no attempt was made to collect data on this larger cell. Instead, the data were collected at −85 °C; even at this temperature, some of the atoms are seen to have large thermal motions, and the bond distances and angles associated with these atoms should be viewed with caution. Compound **2b** underwent some decomposition in the X-ray beam even at −100 °C, and the intensities were adjusted for a 24% decrease in the intensity of standards. Although a linear decay correction was used, it should be pointed out that there is no suitable method of correction for decomposition and therefore the data and the resulting structure, particularly the bond distances and angles, should again be viewed with caution. Structures of compounds **1** and **2b** were solved using direct methods, and refinement information is included in Table VI; final atomic coordinates with additional data (full anisotropic parameters and hydrogen atom positions) are available as supplementary material. In both structures all non-hydrogen atoms were refined anisotropically; hydrogen atoms were calculated in idealized positions and held fixed with isotropic thermal parameters 1.0 greater than those of the attached carbon atoms. In compound **2b** each molecule sits on a 2-fold axis passing through phosphorus atoms P(1) and P(2). The ^{t}Bu methyl groups exhibit large "thermal motion" but did not refine well using a disordered model.

Compound **3** has an orthorhombic unit cell, a = 14.387 (4), b = 36.149 (8), and c = 31.916 (3) Å (T = −70 °C) with extinctions consistent with the unusual space group $C222_1$ (No. 20). Compound **3** has two half-molecules and one solvent molecule (hexane) in the asymmetric unit, but disorder and/or excessive thermal motion combined with a poor data set frustrated attempts to locate many of the carbon atoms. Attempts to refine this structure were abandoned after obtaining R = 0.135, but the Ti, O, Si, and P atomic positions are sufficiently well established to define the structure sketched in Figure 4.

The refinement and analysis of the two structures were carried out using a package of local programs.[30] The atomic scattering factors were taken from the tabulations of Cromer and Waber; anomalous dispersion corrections were by Cromer.[31] In the least-squares refinement, the function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weights, w, assigned as $[\sigma^2(I) + 0.0009I^2]^{-1/2}$.

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Supplementary Material Available: For compounds **1** and **2b** respectively, tables of atomic positions (Tables S1 and S5), anisotropic thermal parameters (Tables S2 and S6), complete bond distances and angles (Tables S3, S4, S7, and S8), and full crystal structure information (Table S9) (15 pages). Ordering information is given on any current masthead page.

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(30) Calabrese, J. C. Central Research and Development, E. I. Du Pont de Nemours and Co., P.O. Box 80228, Wilmington, DE 19880-0228, 1991.

(31) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) Table 2.2B; (b) Table 2.3.1.